

Headline Articles

Unusual Fluorescent Properties of Novel Fluorophores, 6-Aryl-3,4-diphenyl-α-pyrone Derivatives

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Novel fluorophores, 6-aryl-3,4-diphenyl-α-pyrones, were synthesized and their spectroscopic properties investigated in the form of evaporated films on plain glass slides, as well as in the solid and solution states. An electron-donating aryl group on the 6-position of the pyrones causes a red-shift in the absorption and fluorescent maxima. In the solid states, they show intense blue-to-orange fluorescence, but not in solution. This unusual fluorescent property is caused by fixing the 6-aryl group of the pyrones, and is the result of molecular packing. These interactions induce a pathway for radiative decay, which is associated with intense fluorescence emission only in the solid state.

Fluorescent organic compounds have been the focus of considerable interest because of their potential applications to a variety of fields, including their use as fluorescent probes and optoelectronics.[1–3] As a result, the development of a new series of fluorophores has been actively pursued.[4–6] In particular, fluorescence in the solid state represents a major topic of recent research in the area of photofunctional materials, such as fluorescent pigments and electroluminescent devices. Although a variety of readily available organic compounds have been examined, only a few have shown promise for these purposes. Photochemical studies of a series of fluorescent compounds that have well-characterized structures and properties are essential if we are to understand structure-function relationships for such substances.

Among them, some triaryl substituted heterocyclic compounds are known to be organic fluorophores and their properties have been extensively investigated.[7–9] However, photochemical studies of triaryl substituted α-pyrones have not been examined to any extent. The α-pyrone structure is one of basic skeletons found in natural products and is also well-known as a pigment found in yellow flowers.[10–12] α-Pyrones are also useful intermediates in the synthesis of some important hetero- and carbocyclic molecules, including isocarbostyryls, isoquinolines, isochromens, pyridones, and a variety of aromatic compounds.[13–16] In addition, this chromophore has been known to be biologically active since the 1960s, and it was recently found that a low-molecular-weight α-pyrone functions as an inhibitor for HIV-protease, which makes this compound even more interesting from a biological point of view.[17,18]

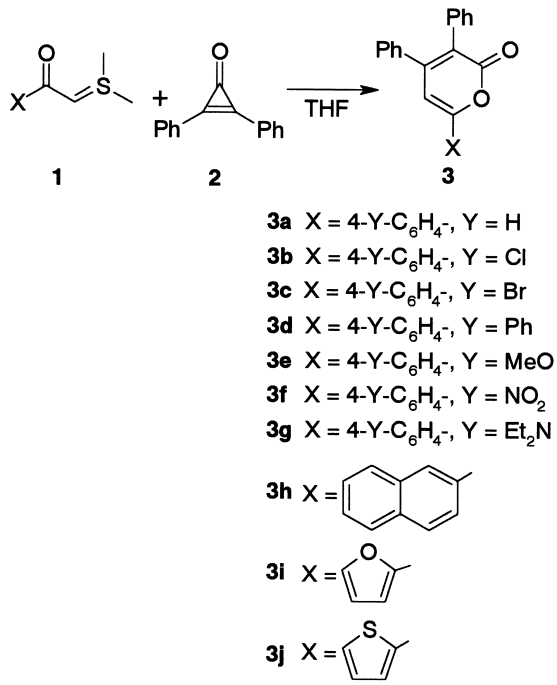
A number of methods for synthesizing these ring systems have been reported[19–23] and reactions of sulfonium or pyridinium ylides and cyclopropenones have been known for the past two decades.[24,25] Of these, however, relatively few have been directed at spectroscopic properties.

We have already reported that 2,3,6-triphenyl-α-pyrone derivatives represent potential candidates for these applications because they show intense fluorescence in the solid state.[26] In this paper, we report on the synthesis of novel functional fluorophores, 6-aryl-3,4-diphenyl-α-pyrone derivatives and their unusual spectroscopic properties.

Results and Discussion

Synthesis of α-Pyrones. The α-pyrone derivatives were synthesized by the reaction of dimethylsulfanium phenacylides **1** with 2,3-diphenylcyclopropenone **2**,[27] as shown in Scheme 1.[24] The sulfonium ylides were prepared in situ from the corresponding sulfonium salts in the presence of a base. A sulfonium salt (0.30 g, 1 mmol) was treated with sodium hydride (60% in oil, 0.04 g, 1 mmol) in THF (10 mL) for 0.5 h at 0 °C to generate the corresponding sulfonium ylide **1**. 2,3-Diphenylcyclopropenone **2** (0.20 g, 1 mmol) was then added and the mixture was stirred for 3 h at ambient temperature. After removal of the solvent in vacuo, the residue was purified by silica-gel column chromatography (hexane/AcOEt = 10/1). The desired compound **3** was obtained as a pale-yellow solid. The yields and melting points of these derivatives are summarized in Table 1.

In the case where the substituent **Y** is an electron-withdrawing group, the yields of **3b** and **3f** were slightly lower than for the other derivatives. It is assumed that the nucleophilicity of sulfonium ylides **1b** and **1f** toward **2** is weak because of their electron-withdrawing substituents. The yields of **3d** and **3h** were also not high, and unreacted materials were recovered in the THF or DMF. Pyrones **3i** and **3j** were obtained in moder-



Scheme 1. Synthesis of 6-aryl-3,4-diphenyl-α-pyrone derivatives.

Table 1. Preparation of 6-Aryl-3,4-diphenyl-α-pyrones (**3**)

	X	Y	Yield/%	Mp/°C
3a	4-**Y**-C_6H_4	H	87	184
3b	4-**Y**-C_6H_4	Cl	69	184
3c	4-**Y**-C_6H_4	Br	80	172
3d	4-**Y**-C_6H_4	Ph	59	203
3e	4-**Y**-C_6H_4	MeO	82	179
3f	4-**Y**-C_6H_4	NO_2	60	228
3g	4-**Y**-C_6H_4	Et_2N	73	219
3h	2-naphthyl	—	63	197
3i	2-furyl	—	62	190
3j	2-thienyl	—	58	210

ate yields.

Spectroscopic Properties of α-Pyrones. The spectroscopic properties of the thus synthesized α-pyrones were evaluated in the solution and solid states, as well as in the form of evaporated films on plain glass slides. Their absorption spectra in acetonitrile and dichloromethane were measured initially. Figure 1 shows the absorption spectra of **3a**, **3e**, **3f**, and **3h** in dichloromethane, and all results are summarized in Table 2. When these compounds dissolved in acetonitrile, they showed a slight blue shift in the absorption maxima by a few nm, compared with spectra obtained in dichloromethane. The absorption maxima of **3e** and **3g**, the **Y** groups of which are electron-donating, were red-shifted, compared with those of **3a**, **3b**, and **3c**. Based on the above facts, we concluded that an intramolecular charge transfer occurs from an electron-donating group to the lactone moiety, which functions as an electron-withdrawing group. Pyrone **3j** showed a larger red-shift in absorption maximum than that of **3h**. This shift is also influenced by the electron-donating properties of the aryl groups. Mizuguchi reported a similar red-shift in the absorption band by an electron-donating group in 8,8-dicyano-3-(4-dimethylaminophenyl)heptafulvene.[28]

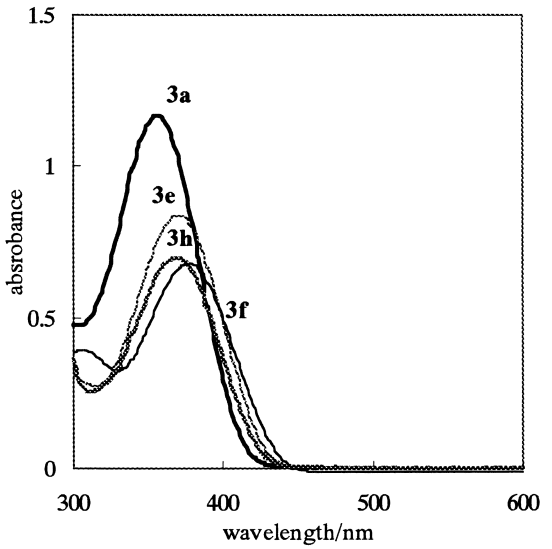


Fig. 1. Absorption spectra of **3a**, **3e**, **3f**, and **3h** in dichloromethane.

Table 2. Spectroscopic Properties of α-Pyrones

	λ_{max}/nm CH_2Cl_2	λ_{max}/nm CH_3CN	λ_{flu}/nm Powder	Relative intensity[a)]
3a	356	357	471	3.2
3b	358	355	479	1.3
3c	359	354	479	1.9
3d	368	364	512	3.1
3e	370	365	521	1.4
3f	378	371	537	0.1
3g	425	421	552	1.2
3h	368	364	509	0.7
3i	372	366	504	0.3
3j	375	371	541	0.3
Alq_3	—	—	511	1.0

a) All compounds were excited at 380 nm.

The absorption maximum of pyrone **3f** in which **Y** is a nitro group, was around 378 nm; this bathochromic shift was larger than that for **3e**.

The electronic structures of the pyrones were calculated using a semi-empirical molecular orbital (MO) method including the CI configuration (AM1 and MOS-F). The results are listed in Table 3. The simulated absorption spectra by MO calculations were blue-shifted, compared to those observed for solutions. The calculated tendency of the substituent effect by the substituent **Y** was similar to those which were experimentally found for solutions. Based on MO calculations, the absorption maximum of **3f** was not unexpected. Figure 2 clearly shows the difference in the direction of the transition dipole moments. The directions of the dipole moments for **3a** and other pyrones are nearly parallel to the carbonyl groups in the pyrones and those of **3f** are parallel to the 4-phenyl group. This fact indicates that the electronic structure of the excited state of **3f** is different from the others. The calculated torsion angle between the pyrone ring and the phenyl group at the 6-position of

Table 3. MO Calculation Results of α-Pyrones[a)]

	λ_{max}	Oscillator	Dipole moment	Torsion
	nm	strength f	debye	angle/deg[b)]
3a	344.02	0.7610	7.193	23.9094
3b	345.31	0.8164	7.926	23.6234
3c	344.25	0.8617	7.112	23.5502
3d	352.39	1.2018	7.235	0.2244
3e	348.44	0.8414	9.026	22.8379
3f	349.92	0.8832	9.420	23.2620
3g	367.03	1.0456	8.140	19.5220
3h	354.86	0.9308	6.883	0.0254
3i	367.55	0.8500	8.700	0.0114
3j	373.44	0.8943	7.296	0.3049

a) Calculated by Win MOPAC 97 (AM1/MOS-F).
b) Angle between pyrone ring andf 6-aryl group.

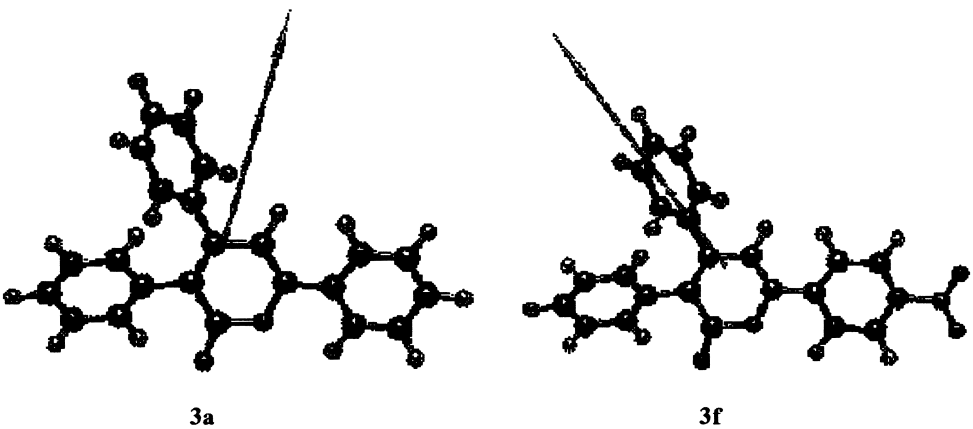


Fig. 2. The directions of transition dipole moments of **3a** and **3f** (by MO calculation).

3a is ca. 24°, which is close to the observed value of 26° obtained by an X-ray structure analysis.[26]

Interestingly, the α-pyrone derivatives emit an intense blue-to-orange fluorescence only in the solid state, but not in solution. Only a few reports in which such a type of fluorescent property is expressed have appeared, as far as we are aware. Tris(8-quinolinolato)aluminum (Alq_3), which is used in electroluminescence devices, showed a similar phenomenon in which an intense fluorescence was observed in the solid state, but was weak in solution. To clarify the utility of α-pyrone derivatives for EL or fluorescent pigment applications, their excitation and emission spectra were measured in powdered form. Samples were injected into the space between two plain glass slides, and their fluorescence was measured using an excitation equal to their absorption maxima in dichloromethane. The relative fluorescent intensities were evaluated by comparing them with that of Alq_3. All of the compounds were excited at 380 nm and the fluorescent intensity of Alq_3 was set as 1. These results are summarized in Table 2 and the fluorescent spectra of **3a**, **3e**, **3h**, and Alq_3 are shown in Fig. 3. The band-shift tendency of those compounds in the solid state was similar to that in the solution state.

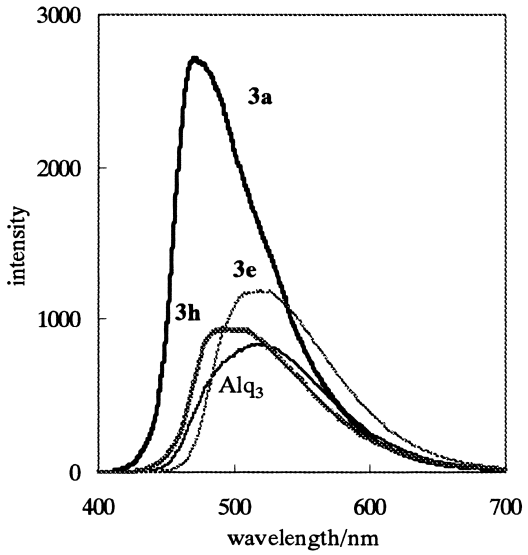


Fig. 3. Fluorescent spectra of **3a**, **3e**, **3h**, and Alq_3 in powdered form.

The fluorescent intensities of the α-pyrones, with the exception of **3f**, were stronger than that of Alq_3. In particular, **3a** and **3d** emit a considerably stronger fluorescence than Alq_3. Therefore, these compounds are of considerable promise for

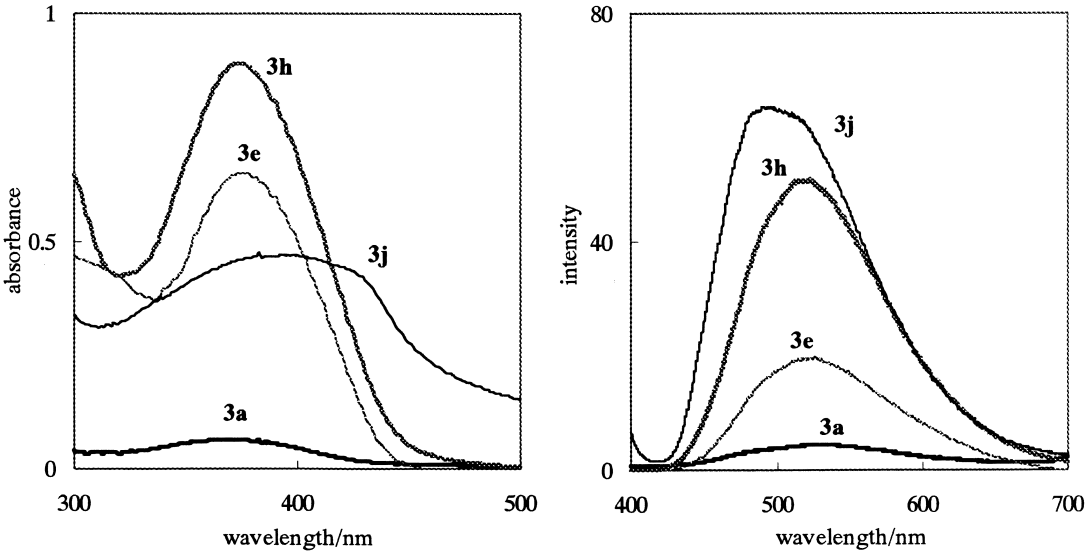


Fig. 4. Absorption (left) and fluorescent (right) spectra of evaporated **3a**, **3e**, **3h**, and **3j**.

use in EL applications, as replacement of Alq_3.

To examine the spectroscopic properties in more detail, evaporated films of these compounds were prepared on plain glass slides using a vacuum evaporation technique. The thickness of the pyrone films was set to about 1000 Å. The absorption and fluorescent spectra were measured and the results are summarized in Table 4. Figure 4 shows the absorption and fluorescent spectra of evaporated **3a**, **3e**, **3h**, and **3j**. The absorption maxima of the pyrone films appeared at longer wavelengths than those in solution, but the effect of the substituent **Y** was similar to that observed for solutions. On the other hand, the fluorescence spectra of evaporated **3a–3h** were also shifted to longer wavelength than those for the powdered form. Pyrone **3a** showed the largest difference in its fluorescent spectra between the evaporated state and the powdered form. The deviation in the fluorescent maxima was ca. 55 nm and the fluorescent intensity of evaporated **3a** was considerably weaker than that of the powdered form. However, after storage for 1 day in a vacuum, **3a** crystallized on the glass slide and the film became muddy and opaque in appearance. As a result, it was not possible to obtain an absorption spectrum, but its emission spectrum changed to nearly the same shape as that observed for the powdered form, as shown in Fig. 5. In order to better understand this type of morphological change, an X-ray diffraction diagram of each of the states of evaporated **3a** was obtained. Figure 6 represents the XRD diagrams of the evaporated **3a** at room temperature before and after crystallization. The diffraction peak before crystallization indicates an amorphous state. Some peaks, the pattern of which corresponds to that of the solid state, were evident after crystallization. This provides clear evidence to show that the initial amorphous phase gradually crystallized during storage. This indicates that the fluorescent spectra of evaporated **3a** in Fig. 5 show the spectral properties of the amorphous and crystal states, respectively. Pyrones **3b**, **3c**, **3d**, and **3g** also exhibited this type of phase alter-

Table 4. Spectroscopic Properties of Evaporated α-Pyrones

	λ_{abs}	λ_{flu}	$\Delta\lambda_{abs}$ [a)]	$\Delta\lambda_{flu}$ [b)]
	nm	nm	nm	nm
3a	371	528	15	57
3b	365	519	7	41
3c	369	516	10	37
3d	375	540	7	16
3e	375	528	5	3
3f	388	522	10	3
3g	429	570	4	23
3h	374	517	6	8
3i	400	498	28	−6
3j	377	517	−2	−24

a) $\lambda_{abs} - \lambda_{max}$ (in CH_2Cl_2).
b) $\lambda_{flu} - \lambda_{flu}$ (in the powdered form).

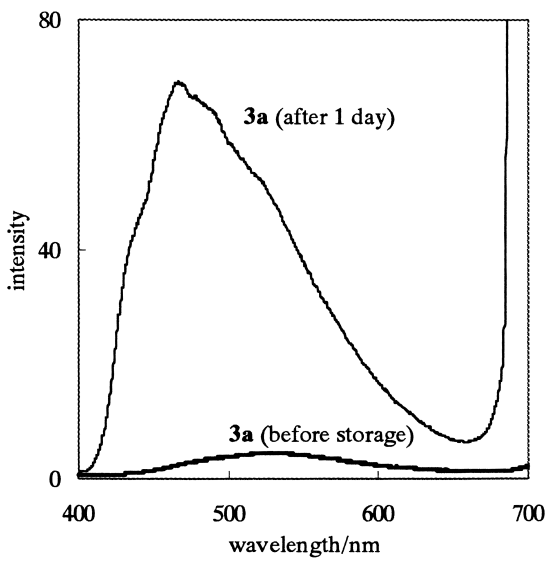


Fig. 5. Changes of fluorescent spectra of evaporated **3a** before and after one-day storage in vacuum.

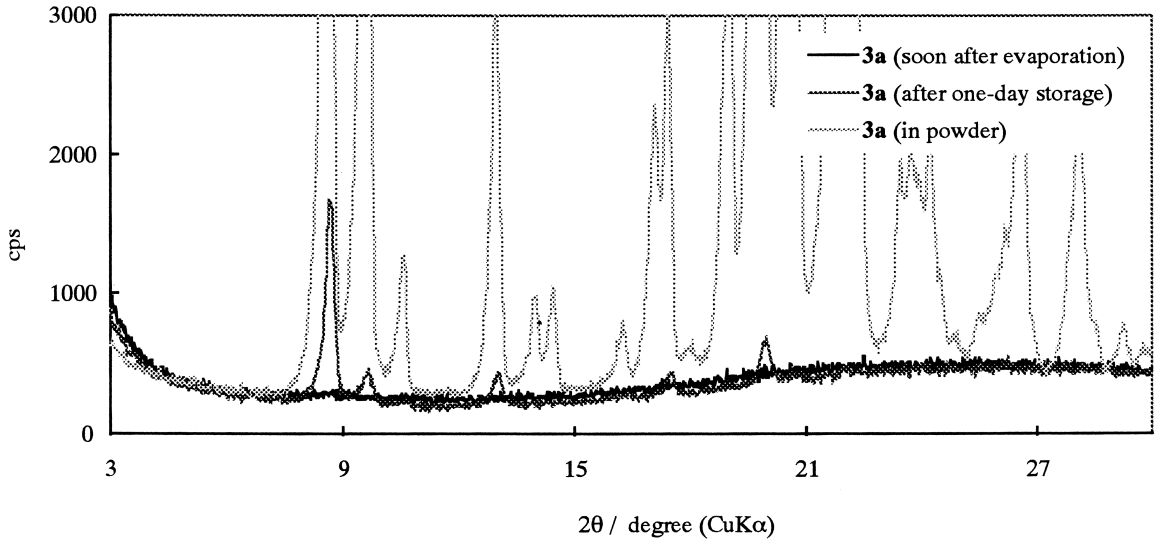


Fig. 6. XRD spectra of evaporated **3a** (soon after evaporation and after one-day storage) and powder form of **3a** as a reference.

nation, but the other pyrones did not. It is known that 3,6-diphenyl-2,5-dihydropyrrolo[3,4-*c*]pyrrole-1,4-dithione shows polymorphismic properties by a vapor treatment.[29] In order to characterize the polymorphismic properties of **3a**, the evaporated film was exposed to vapor of an organic solvent, such as acetone, toluene, and THF, respectively, and the spectral changes were measured after being kept in contact with the saturated vapor for about 1 h. The spectral changes are shown in Fig. 7. In acetone, **3a** crystallized and emitted an intense blue fluorescence, the maximum of which was at 468 nm. In the presence of toluene, **3a** also partially crystallized. In THF, evaporated **3a** remained in an amorphous state, the fluorescent maximum of which was around 528 nm with an intensity that was much weaker than that in the solid state. Crystalline **3a** emitted an intense blue fluorescence; that emitted by the amorphous state was green. This indicates that the strong fluorescence of **3a** is derived from the crystal or solid phase, and the weak fluorescence is the result of the amorphous state. The magnitude of the fluorescence is dependent on the packing interactions in the molecules, i.e. **3a** emits an intense fluorescence in the crystalline state, a weak one in the amorphous state, and none in the solution state. This information supports our previous conclusion concerning the emission of **3a** only in the solid state.[26] The phenyl group at the 6-position of **3a** is fixed at an angle of about 26° to the pyrone plane by molecular packing, and can not rotate freely in the solid state. In the solution state, this phenyl group is able to rotate freely and a pathway involving nonradiative decay is dominant. To confirm this explanation and to characterize the intermolecular interactions in detail, further analyses of these compounds were done based on the X-ray crystal structures.

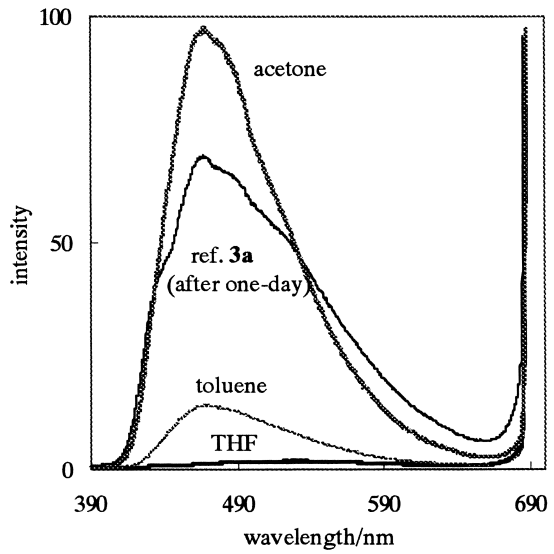


Fig. 7. Fluorescent spectra of evaporated **3a** on vapor treatment in acetone, toluene, and THF and the spectrum after one-day storage as a reference.

X-ray Structure Analysis. X-ray crystallographic analyses were performed on **3a**, **3b**, **3e**, and **3h**. The crystal structure of these four molecules show that the two phenyl groups at the 3- and 4-positions are twisted from the plane of the pyrone ring by about 50°, and that the other aryl group at the 6-position is also twisted out of the pyrone plane, but the angle between these two planes is smaller than those between the other two. Figure 8 shows ORTEP drawings of the crystal structures of **3a**, **3b**, **3e**, and **3h**. Pyrone **3a** consists of two crystallographically independent molecules in the asymmetrical unit. The torsion angles of the 6-phenyl groups on **3a**, **3b**, and **3h** were found to be ca. 26° from the pyrone plane, as shown in Table 5. However, that of **3e** was only 8.1°. This result is in good agreement with our previous expectation that the electron-donating group on **3e** serves to induce an intramolecular charge-transfer state, and that the above torsion angle would be expected to deviate from the others as shown in Table 3.

The molecular packing diagrams of **3a**, **3b**, **3e**, and **3h** clearly show short distances between the molecules, as shown in Fig. 9. The interplaner distance to the nearest molecule was ca. 4 Å.

From these crystallographic results, it can be concluded that the nature of the aryl group is relevant to the unusual fluorescent properties observed, i.e. emission is observed only in the

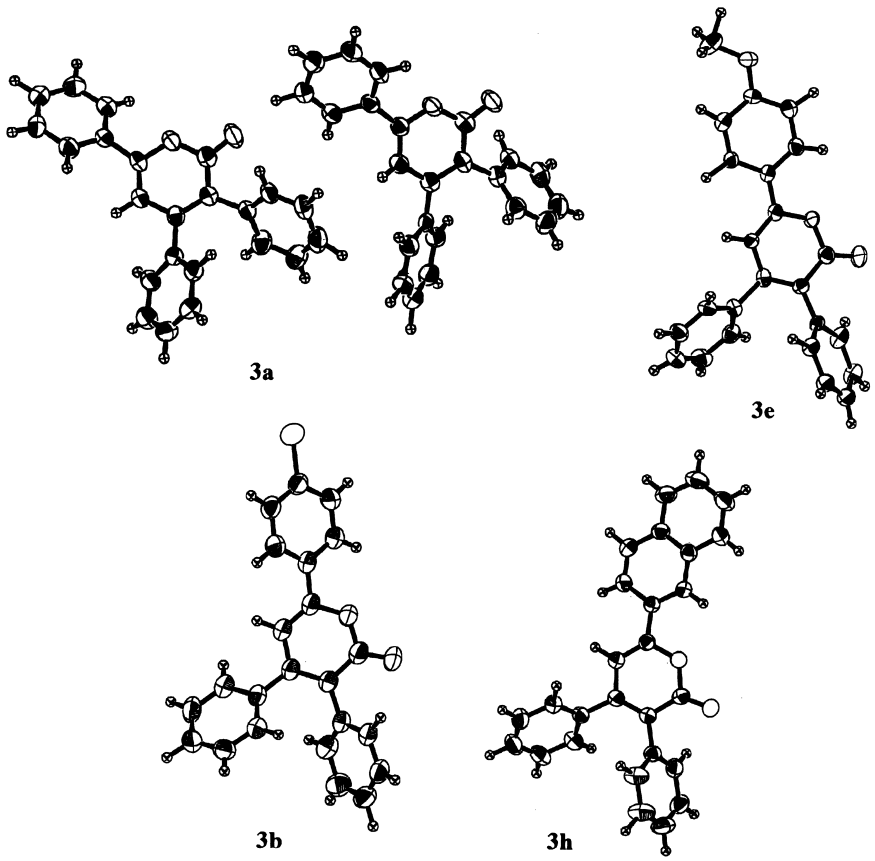


Fig. 8. ORTEP Drawings of **3a**, **3b**, **3e**, and **3h**.

Table 5. Crystallographic Data for **3a**, **3b**, **3e**, and **3h**

	3a	**3b**	**3e**	**3h**
Empirical formula	$C_{23}H_{16}O_2$	$C_{23}H_{15}ClO_2$	$C_{24}H_{18}O_3$	$C_{27}H_{17}O_2$
Fw	324.38	358.82	354.40	373.43
Color	yellow	yellow	yellow	yellow
Habit	prismatic	prismatic	prism	prism
Crystal system	monoclinic	orthorhombic	triclinic	monoclinic
Space group	$P2_1/c$ (#14)	*Pbca* (#61)	$P1$ (#2)	$P2_1/c$ (#14)
a, Å	18.267	19.236	9.860	11.549
b, Å	20.298	20.899	13.275	8.860
c, Å	8.975	8.837	7.306	19.186
α, deg			97.631	
β, deg	90.01		101.721	95.345
γ, deg			99.984	
V, Å^3	3327	3552	908.0	1954.7
Z	8	8	2	4
R	0.062	0.150	0.200	0.046
R_w	0.105	0.077	0.240	0.060
$R1$	0.044	0.046	0.187	0.043
Torsion angle (deg)[a)]	26.2	26.7	8.1	19.4

a) Angle between pyrone ring and 6-aryl group.

solid state. This suggests that the pyrones are densely packed in the crystal forms and that the interplaner distance between the nearest molecules is too short for the 6-aryl group to rotate freely within the single-crystal unit. Therefore, this aryl group is fixed as a result of molecular packing in the solid state, and a pathway involving fluorescence is thus dominant. However, in solution, this interaction becomes weaker, or is lost altogether, and free rotation of the 6-aryl group becomes possible. As a result, a pathway involving nonradiative decay is permitted and the α-pyrone derivatives do not fluoresce in solution.

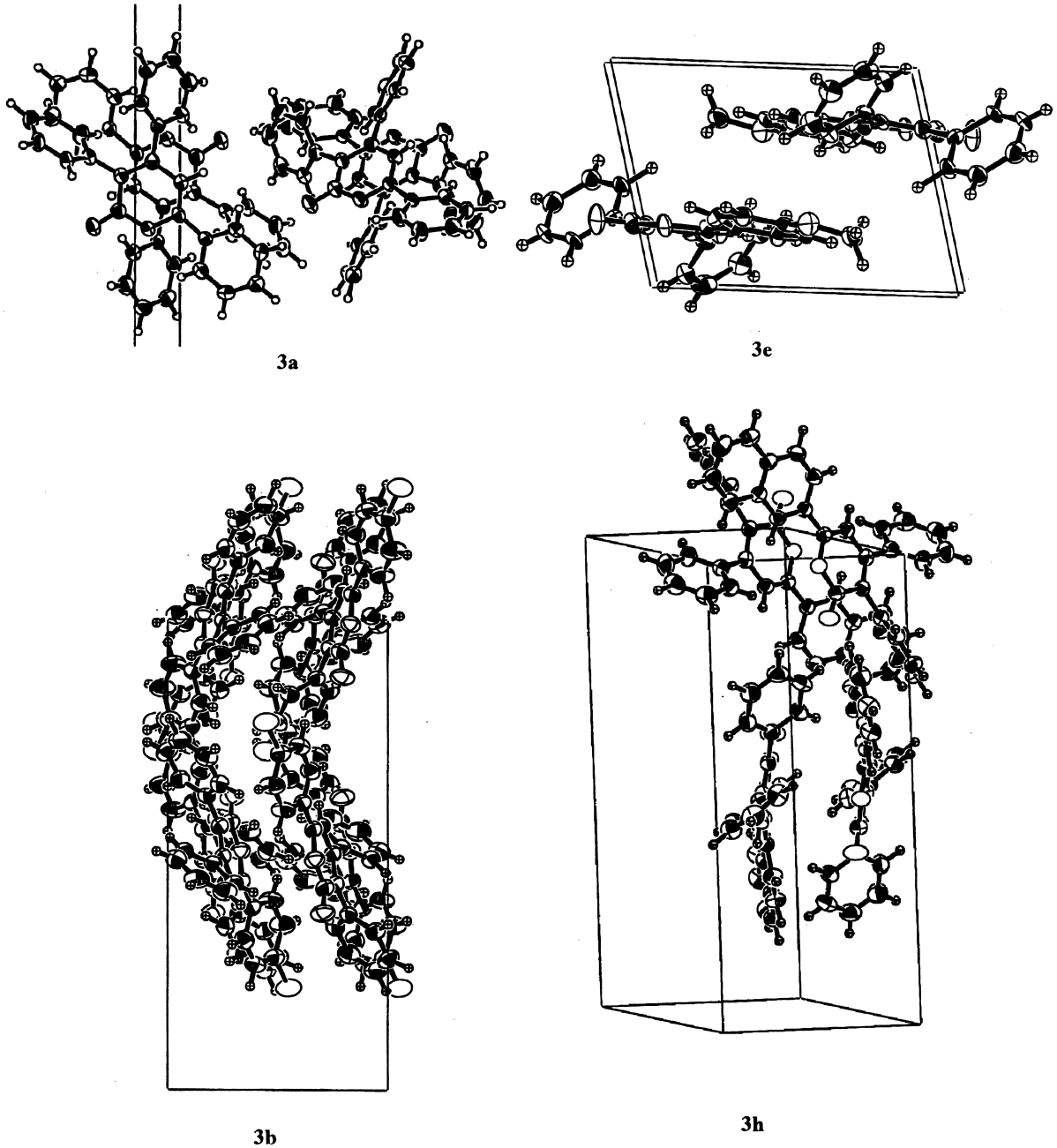


Fig. 9. Molecular packing diagrams of **3a**, **3b**, **3e**, and **3h**.

Conclusions

In conclusion, ten 6-aryl-3,4-diphenyl-α-pyrone derivatives were synthesized and their spectroscopic properties, especially fluorescent properties, were investigated in the solution, amorphous, and solid states. The following conclusions can be drawn from the present investigation:

1. The absorption spectra of solutions of these compounds are influenced by the electronic properties of the aryl group at the 6-position of the pyrones. The electron-donating aryl group causes a red-shift in the absorption maximum, which can be explained by the contribution of the intramolecular charge-transfer state.

2. The fluorescent properties of the pyrones are affected by the magnitude of intermolecular interactions. The strong interaction reduces the interplaner distance of the pyrones in the solid state. This close intermolecular packing induces a pathway involving fluorescence by spatially fixing the aryl group at the 6-position. Therefore, 6-aryl-3,4-diphenyl-α-pyrone derivatives emit an intense fluorescence in the solid states, but only a weak one in the amorphous state and none in solution.

3. The fluorescent materials in the solid state described above have considerable potential for use as a fluorescent pigment and in EL devices.

Experimental

The reagents were obtained commercially (Wako, TCI, or Aldrich), and were used without further purification. The solvents used for spectroscopic measurements were of analytical grade. The melting points were measured with a Yamato MP-S3 apparatus, and are uncorrected. A JASCO FT/IR-410 infrared spectrophotometer was used to record the IR spectra as KBr pellets. Mass spectra were obtained on a Shimadzu GCMS-QP5000 spectrometer and the NMR spectra on a JEOL JNM-EX270 spectrometer. The UV-vis and fluorescent spectra were recorded using a Hitachi U-3300 spectrophotometer and a Hitachi fluorescent spectrophotometer F4500, respectively.

The geometry of the compounds was optimized by means of the AM1 Hamiltonian in MOPAC 97. The MOS-F program was used for all spectroscopic calculations.

The X-ray diffraction diagrams of evaporated films and the powdered form of **3a** were recorded at a rate 0.5°/min using a RINT 2100 from Rigaku Denki.

Single crystals of compounds **3a**, **3b**, **3e**, and **3h** were grown by recrystallization from hexane/ethyl acetate solutions. Data collections for structure analysis were made using an AFC5R and RAX-IS-RAPID Imaging plate diffractometer from Rigaku Denki, and the structures were solved by direct methods.

3,4,6-Triphenyl-α-pyrone (3a). 2-Phenacyl bromide (2.0 g, 10 mmol) and dimethyl sulfide (4 mL, 20 mmol) were stirred at room temperature for 2 h. The resulting white solid was collected by suction filtration and washed with ether. The corresponding sulfonium bromide was obtained as a white solid (2.61 g, 99%). The sulfonium bromide (0.30 g, 1 mmol) was treated with sodium hydride (60% in oil, 0.04 g, 1 mmol) in THF (10 mL) for 0.5 h at 0 °C. 2,3-Diphenylcyclopropenone (0.20 g, 1 mmol) was then added to the solution and the mixture was stirred for 3 h at ambient temperature. After removal of the solvent in vacuo, the residue was eluted from a silica-gel column with hexane/AcOEt (10/1). The desired compound was obtained as a pale-yellow solid (0.30 g, 87%): mp 184 °C; IR (KBr) 1704 cm^{-1}; ^1H NMR ($CDCl_3$, 270 MHz) δ 6.81 (s, 1H), 7.1–7.3 (m, 10H), 7.5 (m 3H), 7.9 (m, 2 H); ^{13}C NMR ($CDCl_3$, 68 MHz) δ 104.9, 123.0, 125.5, 127.8, 128.2, 128.5, 128.8, 130.1, 130.2, 130.6, 130.7, 131.2, 133.6, 137.6, 152.5, 158.1, 162.5; MS *m/z* 324 (M^+); HRMS found: 324.1144, calcd for $C_{23}H_{16}O_2$: 324.1150.

6-(4-Chlorophenyl)-3,4-diphenyl-α-pyrone (3b). To a solution of 4-chlorophenacyldimethylsulfanium bromide (0.30 g, 1 mmol) and sodium hydride (0.04 g, 1 mmol) in THF (10 mL) was added 2,3-diphenylcyclopropenone (0.20 g, 1 mmol), and the solution was stirred at room temperature for 3 h. The reaction mixture was concentrated and the residue was eluted from a silica-gel column with hexane/CH_2Cl_2 (2/1) to afford **3b** as a yellow solid (0.24 g, 67%): mp 184 °C; IR (KBr) 1708 cm^{-1}; ^1H NMR ($CDCl_3$, 270 MHz) δ 6.82 (s, 1H), 7.1–7.3 (m, 10H), 7.44 (d, J = 8.9 Hz, 2H), 7.85 (d, J = 8.9 Hz, 2H); ^{13}C NMR ($CDCl_3$, 68 MHz) δ 105.1, 123.3, 126.7, 127.6, 127.8, 128.3, 128.5, 128.7, 129.1, 129.7, 130.7, 133.5, 136.7, 137.4, 152.4, 156.9, 162.2; MS (CI) 359 (M+1); HRMS found: 358.0760, calcd for $C_{23}H_{15}ClO_2$: 358.0760.

6-(4-Bromophenyl)-3,4-diphenyl-α-pyrone (3c). To a solution of 4-bromophenacyldimethylsulfanium bromide (0.33 g, 1 mmol) and sodium hydride (0.04 g, 1 mmol) in THF (10 mL) 2,3-diphenylcyclopropenone (0.20 g, 1 mmol) was added, followed by stirring at room temperature for 3 h. The reaction mixture was concentrated and the residue was eluted from a silica-gel column with hexane/AcOEt (10/1) to afford **3c** as a yellow solid (0.26 g, 80%): mp 172 °C; IR (KBr) 1708 cm^{-1}; ^1H NMR ($CDCl_3$, 270 MHz) δ 6.83 (s, 1H), 7.1–7.3 (m, 10 H), 7.61 (d, J = 8.6 Hz, 2H), 7.78 (d, J = 8.6 Hz, 2H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 105.3, 123.4, 126.8, 127.4, 127.7, 127.9, 128.3, 128.5, 129.0, 129.6, 130.6, 133.4, 136.6, 137.2, 151.9, 155.7, 161.9; MS *m/z* 402 (M^+), 404 (M+2); HRMS found: 402.0261, calcd for $C_{23}H_{15}BrO_2$: 402.0256.

6-Biphenylyl-3,4-diphenyl-α-pyrone (3d). To a solution of dimethyl(4-phenylphenacyl)sulfanium bromide (0.32 g, 1 mmol) and sodium hydride (0.04 g, 1 mmol) in THF (10 mL) 2,3-diphenylcyclopropenone (0.20 g, 1 mmol) was added, followed by stirring at room temperature for 3 h. The reaction mixture was concentrated and the residue was eluted from a silica-gel column with hexane/AcOEt (10/1) to afford **3d** as a yellow solid (0.23 g, 59%): mp 203 °C; IR (KBr) 1721 cm^{-1}; ^1H NMR ($CDCl_3$, 270 MHz) δ 6.89 (s, 1H), 7.2–7.3 (m, 8H), 7.3–7.5 (m, 5H), 7.64 (m, 2H), 7.71 (d, J = 8.4 Hz, 2H), 7.99 (d, J = 8.4 Hz, 2H); ^{13}C NMR ($CDCl_3$, 68 MHz) δ 104.9, 123.0, 125.9, 127.0, 127.4, 127.6, 127.9, 128.3, 130.0, 130.8, 133.7, 137.7, 139.7, 143.3, 152.6, 157.9, 162.5; MS *m/z* 400 (M^+); HRMS found: 400.1458, calcd for $C_{29}H_{20}O_2$: 400.1463.

6-(4-Methoxyphenyl)-3,4-diphenyl-α-pyrone (3e). To a solution of 4-methoxyphenacyldimethylsulfanium bromide (0.30 g, 1 mmol) and sodium hydride (0.04 g, 1 mmol) in THF (10 mL) 2,3-diphenylcyclopropenone (0.20 g, 1 mmol) was added, followed by stirring at room temperature for 3 h. The reaction mixture was concentrated and the residue was eluted from a silica-gel column with hexane/AcOEt (10/1) to afford **3e** as a yellow solid (0.29 g, 82%): mp 179 °C; IR (KBr) 1708 cm^{-1}; ^1H NMR ($CDCl_3$, 270 MHz) δ 3.88 (s, 3H), 6.73 (s, 1H), 6.98 (d, J = 9.2 Hz, 2H), 7.1–7.3 (m, 10H), 7.86 (d, J = 9.2 Hz, 2H); ^{13}C NMR ($CDCl_3$, 68 MHz) δ 55.5, 103.5, 114.3, 121.7, 123.8, 127.2, 127.4, 127.8, 128.2, 128.5, 130.8, 133.9, 137.9, 138.0, 142.1, 152.9, 158.3, 161.5; MS *m/z* 354 (M^+); HRMS found: 354.1250, calcd for $C_{24}H_{18}O_3$: 354.1259.

6-(4-Nitrophenyl)-3,4-diphenyl-α-pyrone (3f). To a solution of dimethyl(4-nitrophenacyl)sulfanium bromide (0.30 g, 1 mmol) and sodium hydride (0.04 g, 1 mmol) in THF (10 mL) 2,3-diphenylcyclopropenone (0.20 g, 1 mmol) was added, followed by stirring at room temperature for 3 h. The reaction mixture was concentrated and the residue was eluted from a silica-gel column with hexane/CH_2Cl_2 (2/1) to afford **3f** as a yellow solid (0.22 g, 60%): mp 228 °C; IR (KBr) 1707 cm^{-1}; ^1H NMR ($CDCl_3$, 270 MHz) δ 6.98 (s, 1H), 7.1–7.3 (m, 10H), 8.08 (d, J = 8.9 Hz, 2H), 8.33 (d, J = 8.9 Hz, 2H); ^{13}CNMR ($CDCl_3$, 68 MHz) δ 107.5, 124.1, 125.0, 126.2, 127.96, 128.0, 128.4, 128.5, 128.9, 130.6, 133.1, 136.8, 137.0, 148.5, 151.8, 155.1, 161.7; MS *m/z* 369 (M^+); HRMS found. 369.1012, calcd for $C_{23}H_{15}NO_4$: 369.1001.

6-(4-Diethylaminophenyl)-3,4-diphenyl-α-pyrone (3g). To a solution of 4-diethylaminophenacyldimethylsulfanium bromide (0.32 g, 1 mmol) and sodium hydride (0.04 g, 1 mmol) in THF (10 mL) 2,3-diphenylcyclopropenone (0.20 g, 1 mmol) was added, followed by stirring at room temperature for 3 h. The reaction mixture was concentrated and the residue was eluted from a silica-gel column with hexane/AcOEt (10/1) to afford **3g** as a yellow solid (0.29 g, 73%): mp 219 °C; IR (KBr) 1701 cm^{-1}; ^1H NMR ($CDCl_3$, 270 MHz) δ 1.21 (t, J = 6.5 Hz, 6H), 3.42 (q, J = 6.5 Hz, 4H), 6.62 (s, 1H), 6.67 (d, J = 9.2 Hz, 2H), 7.1–7.3 (m, 10H), 7.76 (d, J = 9.2 Hz, 2H); ^{13}C NMR ($CDCl_3$, 68 MHz) δ 12.7, 44.5, 101.5, 111.0, 117.6, 127.1, 127.2, 127.7, 128.1, 128.3, 128.6, 130.9, 134.3, 138.4, 149.4, 153.5, 159.6, 163.1, 172.8; MS

m/z 395 (M^+); HRMS found: 395.5070, calcd for $C_{27}H_{25}NO_2$: 395.5058; Anal. Found:C, 81.67; H, 6.37; N, 3.54%. Calcd for $C_{27}H_{25}NO_2$: C 82.00; H, 6.50; N, 3.54%.

6-(2-Naphthyl)-3,4-diphenyl-α-pyrone (3h). To a solution of dimethyl(2-naphthyl)sulfanium bromide (0.30 g, 1 mmol) and sodium hydride (0.04 g, 1 mmol) in THF (10 mL) 2,3-diphenylcyclopropenone (0.20 g, 1 mmol) was added, followed by stirring at room temperature for 3 h. The reaction mixture was concentrated and the residue was eluted from a silica-gel column with hexane/CH_2Cl_2 (2/1) to afford **3h** as a yellow solid (0.24 g, 63%): mp 197–200 °C; IR (KBr) 1708 cm^{-1}; ^1H NMR ($CDCl_3$, 270 MHz) δ 6.98 (s, 1H), 7.2–7.3 (m, 10H), 7.5 (m, 2H), 7.8–7.9 (m, 4H), 6.98 (m, 1 H); ^{13}C NMR ($CDCl_3$, 68 MHz) δ 105.3, 121.9, 123.1, 126.0, 126.9, 127.5, 127.6, 127.9, 128.3, 128.6, 128.9, 130.8, 133.0, 133.7, 134.1, 137.7, 152.6, 158.0, 162.6; MS *m/z* 374 (M^+); HRMS found: 374.1312, calcd for $C_{27}H_{18}O_2$: 374.1307; Anal. Found: C, 86.34; H, 5.02; N, 0.00%. Calcd for $C_{27}H_{18}O_2$: C 86.61; H, 4.85; N, 0.00%.

6-(2-Furyl)-3,4-diphenyl-α-pyrone (3i). After tetrabutylammonium tribromide (2.41 g, 5 mmol) was added to a solution of 2-acetylfuran (0.55 g, 5 mmol) in CH_2Cl_2 (50 mL) and MeOH (20 mL), the mixture was stirred at room temperature for 1 h until the color of bromine disappeared. After removal of the solvent, the residue was roughly purified by elution from a short silica-gel column with hexane/EtOAc (10/1). The resulting product (0.60 g) and dimethyl sulfide (4 mL, 20 mmol) were stirred at room temperature for 2 h. The resulting white precipitation was collected by suction filtration and washed with ether. The corresponding sulfonium bromide (28%, 2 steps) was obtained as a white solid.

To a solution of dimethyl(2-furyl)sulfanium bromide (0.14 g, 0.5 mmol) and sodium hydride (0.02 g, 0.5 mmol) in THF (5 mL) 2,3-diphenylcyclopropenone (0.10 g, 0.5 mmol) was added, followed by stirring at room temperature for 3 h. The reaction mixture was concentrated and the residue was eluted from a silica-gel column with hexane/AcOEt (7/1) to afford **3i** as a yellow solid (0.08 g, 51%): mp 190 °C; IR (KBr) 1712 cm^{-1}; ^1H NMR ($CDCl_3$, 270 MHz) δ 6.57 (dd, J = 2.7, 3.2 Hz, 1H), 6.77 (s, 1H), 7.08 (d, J = 3.2 Hz, 1H), 7.1–7.3 (m, 10 H), 7.52 (d, J = 2.7 Hz, 1H); ^{13}C NMR ($CDCl_3$, 68 MHz) δ 103.1, 111.7, 112.4, 122.5, 127.5, 127.8, 128.1, 128.5, 128.6, 130.7, 133.7, 137.3, 144.5, 146.4, 150.1, 152.5, 161.7; MS *m/z* 314 (M^+); HRMS found: 314.0940, calcd for $C_{21}H_{14}O_3$: 314.0943.

3,4-Diphenyl-6-(2-thienyl)-α-pyrone (3j). To a solution of dimethyl(2-thienyl)sulfanium bromide (0.14 g, 0.5 mmol) and sodium hydride (0.04 g, 0.5 mmol) in THF (5 mL) 2,3-diphenylcyclopropenone (0.10 g, 0.5 mmol) was added, followed by stirring at room temperature for 3 h. The reaction mixture was concentrated and the residue was eluted from a silica-gel column with hexane/AcOEt (5/1) to afford **3j** as a yellow solid (0.07 g, 44%): mp 210 °C; IR (KBr) 1707 cm^{-1}; ^1H NMR ($CDCl_3$, 270 MHz) δ 6.66 (s, 1H), 7.1–7.3 (m, 11H), 7.46 (dd, J = 2.5, 5.3 Hz, 1H), 7.67 (dd, J = 2.5, 5.3 Hz, 1H); ^{13}C NMR ($CDCl_3$, 68 MHz); δ 104.0, 122.5, 127.3, 127.6, 127.9, 128.3, 128.5, 128.6, 130.8, 133.7, 135.0, 137.5, 140.2, 140.5, 152.7, 153.9, 162.4; MS (CI) *m/z* 330 (M^+); HRMS found: 330.0719, calcd for $C_{21}H_{14}O_2S$: 330.0715.

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